TEMPERATURE DEPENDENCE OF ELECTRICAL PROPERTIES IN REGIOREGULAR POLY(3-HEXYLTHIOPHENE) MODULATED BY CHEMICAL DOPING

S. Ukai, H. Ito, S. Kuroda
Department of Applied Physics, Nagoya University,
Chikusa, Nagoya, 464-8603, Japan.

Abstract

Electrical conductivity and Seebeck coefficient in regioregular poly(3-hexylthiophene) (RR-P3HT) doped with iodine (I_2) have been studied in temperature (T) range from 4.2 K to 300 K and from 77 K to 300 K, respectively. In spite of high doping rate (about 30%), RR-P3HT doped with I_2 shows a semiconductive behavior in view of temperature dependence of both electrical conductivity and Seebeck coefficient. Temperature dependence of electrical conductivity shows charge transport mechanism of thermally activated hopping below doping rate of about 10% and variable range hopping above doping rate of about 10%. Temperature dependence of Seebeck coefficient shows that energy between Fermi level and valence band decreases with increase in doping rate.

1. Introduction

Conjugated polymers are attracting much attention as active components in electronic devices such as light emitting diodes and field effect transistors (FETs). Conjugated polymers can be doped chemically, and then their electrical conductivity varies from insulator to metal [1]. For example, in polyacetylene doped with I_2 and poly(p-phenylenevinylene) doped with AsF_5, metal-insulator transition (MIT) are reported [1, 2, 3]. Increase in electrical conductivity is brought about by increase in mobility of charge carriers [4]. In case of regioregular poly(3-hexylthiophene) (RR-P3HT), mobility of charge carriers increased by electrochemical doping [5], in contrast to many inorganic semiconductors for which mobility decreases with increase in doping rate. Increase in mobility with increase in doping rate may be explained in terms of polaron-bipolaron transition of charge carriers [6]. Recently, we have studied RR-P3HT doped by FET structure with Al_2O_3 as gate insulator [7]. For RR-P3HT doped by field effect, the mobility increased with increase in gate voltage which corresponds to the doping rate in terms of chemical doping. Doping rate of about 4% by field effect was accomplished, but charge transport mechanism is semiconductive. In case of field-effect doping, amount of doping is limited by breakdown voltage of gate insulator. To increase more the amount of doping, chemical doping is needed.

In this study, we doped I_2 into RR-P3HT for doping rate range from 2% to 30% and measured temperature dependence of electrical conductivity in RR-P3HT doped with I_2. We also measured temperature dependence of Seebeck coefficient since thermopower is hard to be influenced by impurities and disorder in polymer structure in contrast to the charge transport on electrical conductivity.

2. Experimental

RR-P3HT (head-to-tail ratio: 98.5%) was purchased from Aldrich Corporation. RR-P3HT was dissolved in $CHCl_3$ solution until saturation (about 20wt%) at room temperature, at 1 atm, under NH_3 gas atmosphere. Then RR-P3HT was drop-cast on mylar film. Thickness of RR-P3HT film was about 1 μm.

For doping rate range from 2% to 10%, doping was carried out by exposing the film to sublimated I_2 [2]. For doping rate range from 10% to 17%, doping was carried out by immersing the film in aqueous solution containing KI (0.50 M) and I_2 [8]. For doping rate range from 17% to 30%, doping was carried out by exposing the film to thermally evaporated I_2 gas. The doping rate was defined as the number of I_5^- per thiophene ring [9]. The number of I_5^- and thiophene ring were calculated from the weight of RR-P3HT film before and after doping. Doping rate of more than 30% could not been achieved by any method.

Electrical conductivity was measured with a Keithley 2000 digital multimeter in temperature range from 4.2 K to 300 K under low vacuum (about 0.1Pa). Seebeck coefficient was measured with a HP34420A digital nanovoltmeter in temperature range from 77 K to 300 K under low vacuum (about 0.1Pa) using Cu-constantan thermocouples. Typical temperature gradient was set about 3 K.

3. Results and Discussion

3.1 Electrical conductivity measurement.
Fig. 1 shows temperature dependence of electrical conductivity in the range from 4.2 K to 300 K. At each of doping rate, RR-P3HT doped with I_2 indicates semiconductive behavior in which electrical conductivity decreases with decrease in temperature. In spite of high doping rate as much as 30%, RR-P3HT doped with I_2 did not turn into metal. Recently, Yamamoto reported that pressed RR-P3HT powder doped with I_2 showed metallic behavior [10], and Fukuhara also reported that pressed poly(3-methylthiophene) powder doped with PF_6^- showed metallic behavior [11]. According to their results, it is nesesarry to apply pressure in addition to the high doping rate to obtain metallic behavior of RR-P3HT.

Conductivity of semiconductive polymers is explained in terms of thermally activated hopping given by

$$\sigma = \sigma_o \exp(-\frac{E_A}{k_B T}) \qquad [1]$$

where σ_o is a constant, E_A is an activation energy, k_B is Boltzmann constant. In this case, charge carriers are activated by thermal energy from traps, and hop to the nearest site. At low doping rates (2% -10%), the conductivity obeys eq. [1] as shown in Fig. 2 (a). At high doping rates of more than 10%, the conductivity is more likely to be explained in terms of variable range hopping given by

$$\sigma = \sigma_o \exp(-(\frac{T_o}{T})^{\frac{1}{4}}) \qquad [2]$$

where T_o is constant, as shown in Fig. 2 (b). In this case, charge carriers hop to sites of equal energy with the help of tunnel effect, implying larger density of state at Fermi level. Transformation of charge transport mechanism from thermally activated hopping to variable range hopping with increase in doping rate may indicate increase in density of state at Fermi level.

3.2 Seebeck coefficient measurement.

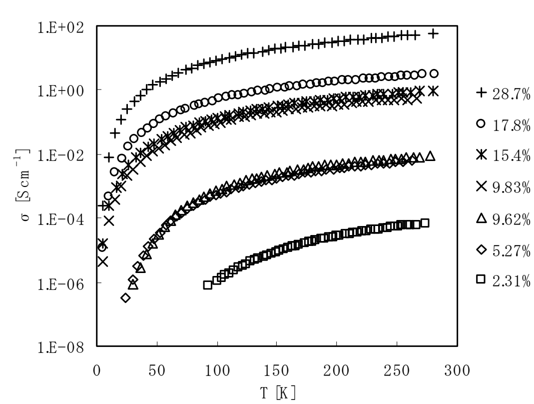

Fig. 1. Temperature dependence of electrical conductivity in RR-P3HT doped with I_2.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **JUL 2004**	2. REPORT TYPE **N/A**	3. DATES COVERED **-**

4. TITLE AND SUBTITLE **Temperature Dependence of Electrical Properties in Regioregular Poly (3-Hexylthiophene) Modulated by Chemical Doping**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **AOARD/AFOSR Unit 45002 APO AP 96337-5002**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
Proceedings of the International Conference for the Science and Technology of Synthetic Metals (ICSM 2004). Held in New South Wales, Australia on Jun 28- July 2 2004. Copyrighted: Government Purpose Rights License. See also ADM001811.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**UU**	**2**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

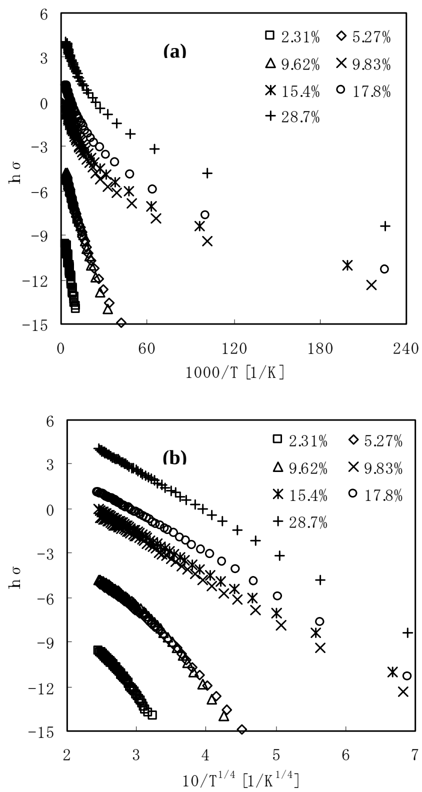

Fig. 2. (a) T^{-1} and (b) $T^{-1/4}$ dependence of electrical conductivity for RR-P3HT doped with I_2.

Fig. 3 shows temperature dependence of Seebeck coefficient in the range from 77 K to 300 K. Seebeck coefficients are positive at each doping rate, indicating that charge carriers in RR-P3HT doped with I_2 are positive carriers. Although Seebeck coefficient decreases with increase in doping rate, RR-P3HT doped with I_2 is semiconductive even at high doping rate as much as 25%. Temperature dependence of Seebeck coefficient for semiconductor is explained by

$$S = \frac{k_B}{q}\left(\frac{E_F - E_V}{k_B T} + \frac{5}{2} + r\right) \quad [3]$$

where q is the electron charge, E_F and E_V are energies at Fermi level and valence band, respectively, r is constant which is generally either -1/2 or +3/2. Fig. 4 shows relation between E_F - E_V and doping rate. E_F - E_V decreases with increase in doping rate. This agrees with the change in activation energy of mobility observed for field-effect doping [7]. Doping rate of about 10% seems to be the inflection point, decrease in E_F - E_V gradually accelerates before this point and decelerates after this point. This is in agreement with the doping rate at which the transformation of charge transport mechanism from thermally activated hopping to variable

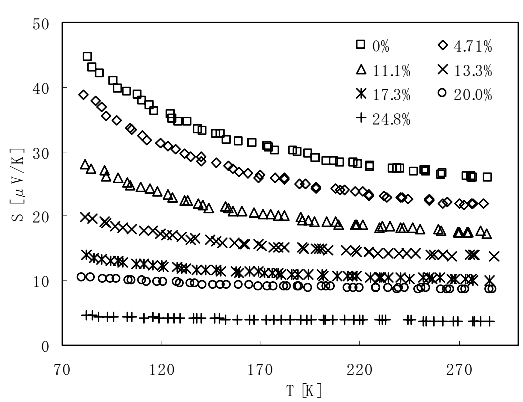

Fig. 3. Temperature dependence of Seebeck coefficient in RR-P3HT doped with I_2.

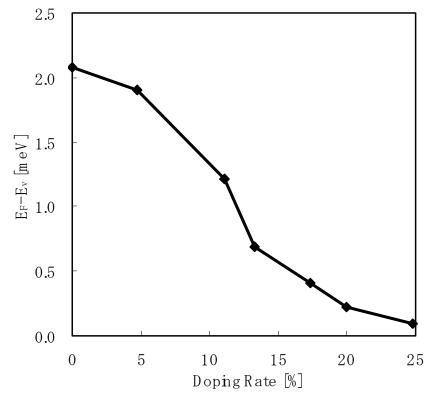

Fig. 4. Relation between E_F - E_V and doping rate in RR-P3HT doped with I_2.

range hopping occurs. It is possible that polaron-bipolaron transition occurs at doping rate of about 10%.

4. Conclusion

We have measured temperature dependencies of electrical conductivity and Seebeck coefficient in RR-P3HT doped with I_2. Temperature dependencies have proved that RR-P3HT doped with I_2 remains semiconductive even at high doping rate. By analyses of temperature dependence of electrical conductivity, charge transport mechanism is explained by the thermally activated hopping in low doping rate (2% - 10%) and variable range hopping in high doping rate (10% - 30%).

Acknowledgement

We thank T. Ishiguro for providing an experimental apparatus for us.

References

[1] A. J. Heeger, S. Kivelson, J. R. Schieffer and W-. P-. Su, Solitons in conducting polymers, Rev. Mod. Phys. 60 (1988) 781-847.
[2] H. Kaneko, T. Ishiguro, J. Tsukamoto and A. Takahashi, Low temperature magnetoresistance of iodine-doped polyacetylene in metal-nonmetal transition region, J. Phys. Soc. Jpn. 62 (1993) 3621-3632.
[3] J. M. Madsen, B. R. Johnson, X. L. Hua, R. B. Hallock, M. A. Masse and F. E. Karasz, Temperature dependence of the electrical conductivity of arsenic pentafluoride-doped poly(p-phenylene vinylene), Phys. Rev. B 40 (1989) 11751-117555.
[4] Y. Kunugi, Y. Harima, K. Yamashita, N. Ohta and S. Ito, Charge transport in a regioregular poly(3-octylthiophene) film, J. Mater. Chem. 10 (2000) 2673-2677.
[5] X. Jiang, Y. Harima, K. Yamashita, Y. Tada, J. Ohshita and A. Kunai, A transport study of poly(3-hexylthiophene) films with different regioregularities, Synth. Met. 135-136 (2003) 351-352.
[6] M. Kuwabara, Y. Shimoi and S. Abe, Polaron versus bipolaron in conducting polymers: a density matrix renormalization group study, J. Phys. Soc. Jpn. 67 (1998) 1521-1527.
[7] S. Ukai, H. Ito and S. Kuroda, Mobility of charge carriers in regioregular poly(3-hexylthiophene) induced by field-effect transistor with Al_2O_3 as gate insulator, Jpn. J. Appl. Phys. 43 (2004) 366-371.
[8] D. Komarudin, A. Morita, K. Osakada and T. Yamamoto, Iodine doping of poly(thiophene-2,5-diyl) and poly(3-alkylthiophene-2,5-diyl)s in aqueous media, Polym. J. 30 (1998) 860-862.
[9] H. Sakai, M. Mizota, Y. Maeda, T. Yamamoto and A. Yamamoto, Resonance Raman and iodine-129 Moessbauer spectroscopic study odf iodine doped in polythiophene, Bull. Chem. Soc. Jpn. 58 (1985) 926-931.
[10] T. Yamamoto, M. Abla, T. Shimizu, D. Komarudin, B.-L. Lee and E. Kurokawa, Temperature dependent electrical conductivity of p-doped poly(3,4-ethylenedioxythiophene) and poly(3-alkylthiophene)s, Polym. Bull. 42 (1999) 321-327.
[11] T. Fukuhara, S. Masubuchi and S. Kazama, Pressure-induced metallic resistivity of PF_6^- doped poly(3-methylthiophene), Synth. Met. 92 (1998) 229-233.